PURGE-AND-TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

The method used for the analysis of volatile organic compounds (VOCs) and volatile and semi-volatile disinfection by-products was a purge-and-trap (P&T) gas chromatography (GC)/ mass spectrometry (MS) method based on U. S. Environmental Protection Agency (USEPA) Method 524.2 (Figure 1). The methods development included the addition of several volatile and semi-volatile DBPs and some changes to the GC conditions (i.e., analytical column and column temperature program).

EXPERIMENTAL

Instrumentation

The instrument used was a Varian Saturn 2000 mass spectrometer (Varian Analytical Associates Inc., Walnut Creek, CA) equipped with a 3800 gas chromatograph (GC). A Tekmar LSC2000 concentrator (Tekmar Co., Cincinnati, OH) and a Varian Archon P&T autosampler (Varian) were used for automated sampling.

Sample Preparation

Information about the analytical standards used for this P&T method are outlined in Table 1. Standard mixes were obtained from Ultra Scientific (North Kingstown, RI), which contained the following compounds at a level of 5000 µg/mL each in acetone: dichloro-, bromochloro-, dibromo-, and trichloroacetonitrile, 1,1-dichloro- and 1,1,1-trichloropropanone, and chloropicrin. The trihalomethane mix (Ultra Scientific) contained chloroform, bromodichloromethane, dibromochloromethane, and bromoform at a level of 5000 µg/mL each in methanol. Each of the VOCs was prepared from separate, individual solutions containing chloromethane, bromomethane, dibromomethane, bromochloromethane, carbon tetrachloride, methyl *tertiary* butyl ether, and methyl ethyl ketone, all of which were obtained from Supelco (Bellefonte, PA) at either a 2000 or 5000 µg/mL level. An EPA Method 524.2 Fortification Solution (Supelco) contained the internal standards for this analysis, fluorobenzene (FB), and the surrogates, 4-bromofluorobenzene (BFB) and 1,2-dichlorobenzene-d_4 (1,2-DCP-d_4), at concentrations of 2000 µg/mL each in methanol. The other target DBPs were obtained in the highest purity available from sources listed in Table 1.

Stock Solutions from Neat Compounds

For all of these new, target DBPs that were being investigated in this project, stock solutions were prepared by either of two different methods. First, those DBPs that were prepared from pure, neat compound as follows. An accurately measured portion of 1.0 mL of methanol solvent (Burdick & Jackson, purge and trap grade, Muskegon, MI) was placed into a capped 2.0 mL autosampler vial and weighed. Approximately 2-3 µL of the neat compound was pulled into a cleaned syringe and spiked into the solvent after piercing the septum. The additional weight by difference, between 2-5 mg, was used to calculate the concentration of each compound. The septum caps were changed before storage. Alternatively, those DBPs that were solid were prepared by weighing the standard in the autosampler vial and adding solvent.

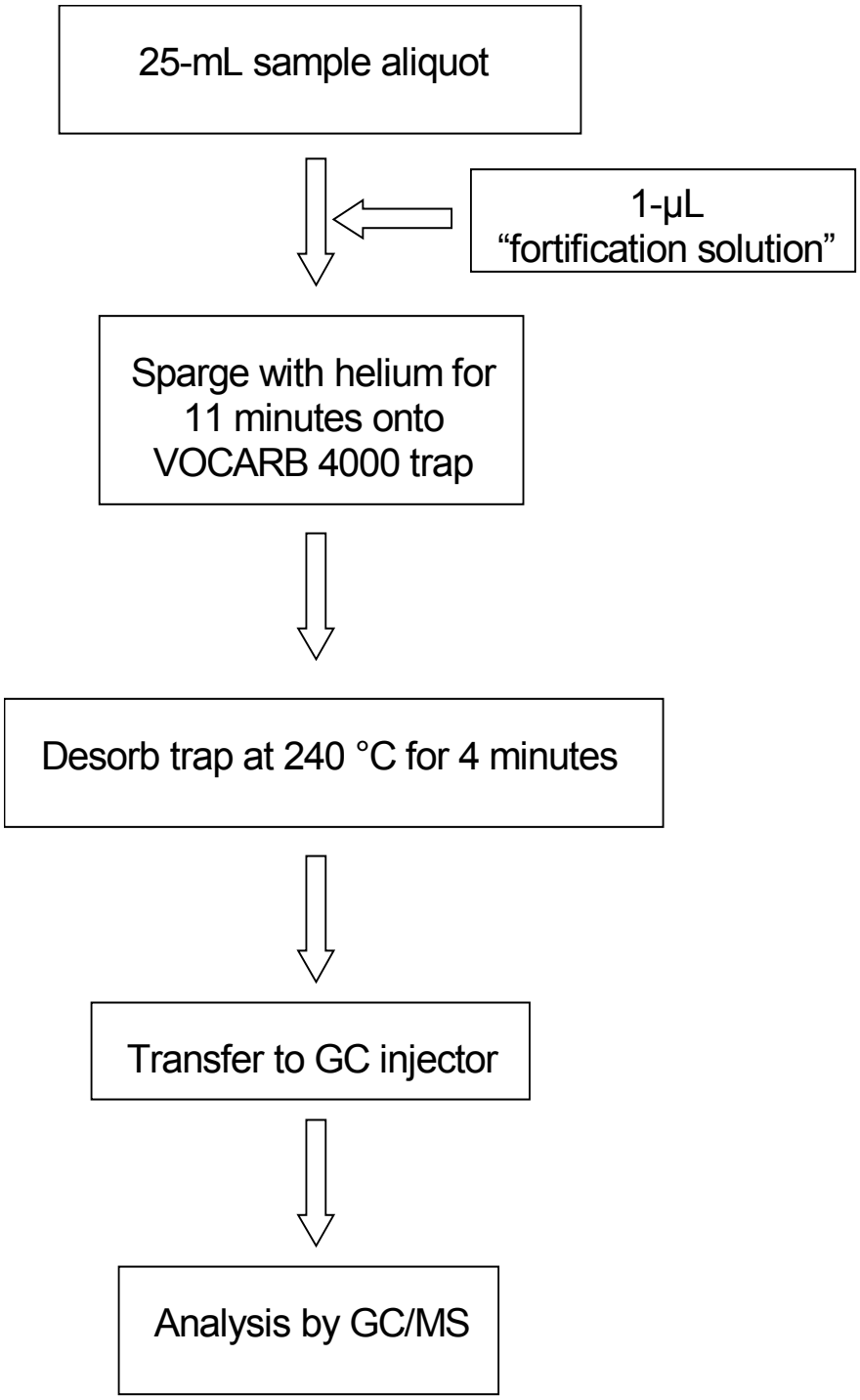

Figure 1. Summary of the Purge and Trap-GC/MS method used for analyzing DBPs in drinking water.

Standard Spiking Solutions

A standard DBP spiking solution was prepared by diluting all of the target compounds to a final volume of 1 mL of methanol (Burdick & Jackson). Table 2 outlines the concentrations and volumes of the standard solutions used to prepare the DBP spiking solution. This solution was used to prepare P&T calibration standards.

Internal Standard and Surrogates

The internal standard and surrogates were prepared as follows. Into a 5-mL volumetric flask was measured 4.5 mL of methanol. A 62.5 µL aliquot of the "fortification solution" was added to the methanol and the volume brought up to 5 mL. This solution was then transferred to the Archon autosampler standard solution reservoir. The Archon autosampler then adds a 1 µL standard addition to the sample water prior to purge-and-trap concentration for a final concentration of 1 µg/L.

Calibration Standards and Check Samples

Calibration standards were prepared at the levels of 0.2, 0.5, 1.0, 2.5, 5.0, 10, 20, and 40 µg/L. An appropriate amount of the DBP spiking solution was added to a 50-mL volumetric flask containing purified water (Ultra Resi-analyzed, J.T. Baker, Phillipsburg, NJ). This solution was then transferred to a 40-mL vial containing 2 drops of 1 M H_2SO_4 to bring the pH down to 3-3.5, then capped with an open-top cap and Teflon-silicon septa. Calibration standards were prepared every time a set of samples was analyzed, approximately every two weeks.

Check standards were analyzed at the beginning and end of each analytical run. These check standards were prepared in the same way as calibration standards, but at the 5 or 10 µg/L level.

Table 1. P&T-GC/MS DBP target analyte sources

Compound Class/DBP	Source	Compound Class/DBP	Source
THM Mix	Ultra Scientific[a]	Halonitromethanes	
Chloroform		Chloronitromethane	Can Syn[e]; Helix
Bromodichloromethane		Bromonitromethane	Aldrich
Dibromochloromethane		Dichloronitromethane	Can Syn; Helix
Bromoform			
		Haloacetonitriles	
551B Mix	Ultra Scientific	Chloroacetonitrile	Aldrich
Dichloroacetonitrile		Bromoacetonitrile	Aldrich
Bromochloroacetonitrile			
Dibromoacetonitrile		VOCs	
1,1-Dichloropropanone		Chloromethane	Supelco[g]
1,1,1-Trichloropropanone		Bromomethane	Supelco
Chloropicrin		Dibromomethane	Supelco
		Bromochloromethane	Supelco
Iodomethanes		Carbon tetrachloride	Supelco
Dichloroiodomethane	AGBAR[b]	MTBE	Supelco
Bromochloroiodomethane	AGBAR	MEK	Supelco
Dibromoiodomethane	AGBAR		
Chlorodiiodomethane	AGBAR	Miscellaneous	
Bromodiiodomethane	AGBAR	Benzyl chloride	Fluka
Haloketones		Internal Standard	
Chloropropanone	Aldrich[f]	Fluorobenzene	Supelco
1,3-Dichloropropanone	Aldrich		
1,1,3-Trichloropropanone	Fluka[h]	Surrogates	
1,1-Dibromopropanone	UNC[c]; Helix[d]	4-Bromofluorobenzene	Supelco
		1,2-Dichlorobenzene-d_4	Supelco

[a]Ultra Scientific (North Kingstown, R.I.)
[b]AGBAR: Aigues of Barcelona (Spain)
[c]UNC: Synthesized by University of North Carolina at Chapel Hill
[d]Helix Biotech (New Westminster, B.C., Canada)
[e]Can Syn: Synthesized by Can Syn Chem Corp. (Toronto, ON, Canada)
[f]Aldrich (St. Louis, Mo.)
[g]Supelco (Bellefonte, Pa.)
[h]Fluka (St. Louis, Mo.)

Table 2. Standard spiking solution preparation

Compound	Abbrev. Name	Conc. (mg/L)	Purity	Adjusted Conc. (mg/L)	Actual Transfer Vol. (uL) 50 mg/L Std	Final Concentration (50 mg/L Std)
THM/551B Mix						
Chloroform	TCM	5000	99+%	5000	10	50
Bromodichloromethane	BDCM	5000	99+%	5000	10	50
Dibromochloromethane	DBCM	5000	99+%	5000	10	50
Bromoform	TBM	5000	99+%	5000	10	50
EPA 551B Mix						
Dichloroacetonitrile	DCAN	5000	99+%	5000	10	50
Bromochloroacetonitrile	BCAN	5000	99+%	5000	10	50
Dibromoacetonitrile	DBAN	5000	99+%	5000	10	50
1,1-Dichloropropanone	1,1-DCP	5000	99+%	5000	10	50
1,1,1-Trichloropropanone	1,1,1-TCP	5000	99+%	5000	10	50
Chloropicrin	TCNM	5000	99+%	5000	10	50
Iodomethane Mix						
Dichloroiodomethane	DCIM	3500	93.3%	3250	17	55.25
Bromochloroiodomethane	BCIM	5200	96.7%	5050	9.9	49.995
Dibromoiodomethane	DBIM	3400	97.2%	3300	15	49.5
Chlorodiiodomethane	CDIM	4200	86.3%	3600	14	50.4
Bromodiiodomethane	BDIM	4800	91.5%	4400	11	48.4
Haloacetonitrile Mix						
Chloroacetonitrile	CAN	3700	99+%	3700	13.5	49.95
Bromoacetonitrile	BAN	5700	99+%	5700	9	51.3
Haloketone Mix						
Chloropropanone	CP	2700	98.1%	2650	19	50.35
1,3-Dichloropropanone	1,3-DCP	4100	99+%	4100	12	49.2
1,1,3-Trichloropropanone	1,1,3-TCP	3500	97.7%	3400	15	51
1,1-Dibromopropanone	1,1-DBP	3300	94.1%	3100	16	49.6
Halonitromethane Mix						
Chloronitromethane	CNM	2700	98.8%	2650	19	50.35
Bromonitromethane	BNM	5200	99+%	5200	10	52
Dichloronitromethane	DCNM	5000	99+%	5000	10	50
Miscellaneous						
Benzyl chloride	BC	3100	99+%	3100	16	49.6
Volatiles Mix						
Chloromethane	ClMe	2000	99+%	2000	25	50
Bromomethane	BrMe	2000	99+%	2000	25	50
Dibromomethane	DBM	2000	99+%	2000	25	50
Bromochloromethane	BCM	2000	99+%	2000	25	50
Carbon Tetrachloride	CCl4	5000	99+%	5000	10	50
MtBE		2000	99+%	2000	25	50
MEK		2000	99+%	2000	25	50

Gas Chromatography

A DB-624 GC column was used (30-m, 0.25-mm ID, 1.4-µm film thickness) (J & W Scientific/Agilent, Folsom, CA). The 1079 injector was set at 220 °C with a split ratio of 30:1. The column temperature program used was developed for a wide range of VOCs: an initial oven temperature of 35 °C, which was held for 4 minutes, followed by an increase at a rate of 4 °C/min to 50 °C, with no time hold, followed by an increase at a rate of 10 °C/min to 175 °C, which was held for 2 min, then a final increase at a rate of 20 °C/min to 200 °C, which was held for 1.5 min. The total temperature run time was 25 min. This temperature program was used until January 2002.

For analyses performed after June 2001, a DB-1 GC column was used (30-m, 0.25-mm ID, 1-µm film thickness) (J & W Scientific/Agilent), and the 1079 injector was set at 220 °C with a split ratio of 20:1. The same column temperature program that was used with the DB-624 column was used with the DB-1 column. A modified temperature program was used beginning in January 2002 to match the work that was developed for the LLE-GC/ECD method: isothermal column temperature at 35 ºC held for 23 min, followed by an increase at a rate of 4 ºC/min to 139 ºC, with no time hold, followed by an increase at a rate of 27.7 ºC/min to a final temperature of 250 ºC, which was held for 5 min. Total run time was 58.0 min.

Mass Spectrometry

Electron ionization (EI) was used on the Saturn GC/mass spectrometer. Table 3 outlines the mass spectrometer parameters used for this method.

Purge-and-Trap (P&T) Analysis

The P&T concentration was carried out using the Varian Archon autosampler, which prepared a 25 mL aliquot of sample for transfer to the Tekmar LSC 2000 concentrator. The 40-mL sample vials were placed in the Archon autosampler, where a 25-mL aliquot was taken. Prior to transfer to the LSC 2000, 1 µL of the "fortification solution" was added. Once the sample was transferred to the LSC 2000 concentrator, it was sparged for 11 min at room temperature with helium, at a flow rate of 15 mL/min, onto a VOCARB 4000 trap (Supelco). The analysis continued with a desorption preheating of the trap to 240 °C and final desorption of the sample for 4 min. At this point the sample was then "injected" onto the Varian GC attached to the Saturn mass spectrometer.

Sample Preservation

Samples were collected in nominal 40-mL vials with Teflon-faced silicon septa and polypropylene open-top screw caps. The sample vials were filled with 1.4 mg of ascorbic acid to quench any residual oxidant present at the time of sampling. A solution of freshly prepared sulfuric acid was used to reduce the pH to within the 3-3.5 range to provide stability of the target analytes and was added prior to capping the sample bottle. This reduction in pH was necessary in order to eliminate the possibility of base-catalyzed hydrolysis that many of the target analytes are susceptible to at higher pH. Samples were stored during transit to the laboratory in ice chests with ice-packs to keep them cold. Upon arrival at the laboratory, the samples were placed in a 10 °C refrigerator for longer-term storage.

Table 3. Saturn ion trap mass spectrometer conditions

Segment 1	filament off, no data acquisition			
Segment 2	start time	1.0 min.		
	end time	50 min.		
	emission current	25 µA		
	scan time	1.00 sec		
	low mass	41 m/z		
	high mass	400 m/z		
	ionization mode	EI AGC [1]		
	ion preparation technique	none		
	EI auto mode:			
		Mass range	ion. storage level	ion. time factor
	scan segment 1	10 to 70	35 m/z	120%
	scan segment 2	71 to 78	35 m/z	70%
	scan segment 3	79 to 150	35 m/z	100%
	scan segment 4	151 to 650	35 m/z	68%
	maximum ionization time	25000 µsec		
	target TIC	30000 counts		
	prescan ionization time	100 µsec		
	background mass	45 m/z		
	RF dump value	650 m/z		

[1] AGC - automatic gain control

RESULTS AND DISCUSSION

Detection Limits

Detection limits were determined in two different ways. The first was strictly by observing the lowest level standard that could be seen and measuring the peak area counts. Based on a signal-to-noise ratio of 5 or greater, a detection limit was initially used. This technique resulted in a wide variety of observed levels for each of the target analytes. The second method used was a statistical evaluation of seven replicates run on two successive days. This method yielded significantly higher detection limits for the target analytes. The method detection limit (MDL) was determined for each analyte as follows:

MDL = t (S)
t = 2.65 (student t value for 13 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 14 replicate analyses

These MDLs were used as minimum reporting levels (MRLs), except where the instrumental detection limit proved to be higher. Often, the MRLs corresponded to the lowest level standard on the calibration curve. Table 4 shows the DL and MDL for each of the P&T target compounds. Where NA is reported for a compound, the opportunity to calculate the MDL was not available, as the compound was added very late in the project for P&T analysis. This table shows that these compounds are amenable to P&T analysis.

Table 4. Detection limits for purge-and-trap DBP analysis

Compound	DL (µg/L)	MDL (µg/L)	Compound	DL (µg/L)	MDL (µg/L)
Chloroform	0.2	0.684	Chloromethane	0.2	0.903
Bromodichloromethane	0.2	0.732	Bromomethane	0.2	1.02
Dibromochloromethane	0.2	0.727	Dibromomethane	0.5	0.775
Bromoform	0.5	0.716	Bromochloromethane	0.5	0.654
			Carbon Tetrachloride	0.2	0.906
Dichloroacetonitrile	0.2	0.945	MtBE	0.2	0.721
Bromochloroacetonitrile	0.5	NA	Methyl ethyl ketone	0.5	0.617
Dibromoacetonitrile	0.5	NA			
1,1-Dichloropropanone	0.5	0.775	Chloropropanone	0.5	1.19
1,1,1-Trichloropropanone	0.5	0.755	1,3-Dichloropropanone	0.5	NA
Chloropicrin	0.5	NA	1,1,3-Trichloropropanone	0.5	NA
			1,1-Dibromopropanone	0.5	NA
Dichloroiodomethane	0.5	0.819			
Bromochloroiodomethane	0.5	0.748	Chloronitromethane	0.5	NA
Dibromoiodomethane	0.5	1.28	Bromonitromethane	0.5	NA
Chlorodiiodomethane	0.5	0.669	Dichloronitromethane	0.5	NA
Bromodiiodomethane	0.5	0.811			
			Chloroacetonitrile	0.2	0.775
Benzyl chloride	0.5	0.624	Bromoacetonitrile	2.5	1.12

DL = detection limit; MDL = method detection limit

Evaluation of Analytical Columns

A DB-624 column was initially installed on the Saturn GC/MS in the early phase of the project. This was due to the fact that the instrument was shared with another group analyzing VOCs for compliance purposes. As the project progressed, it was determined that other arrangements needed to be made in order to accommodate the addition of analyzing solid phase extraction (SPE) samples on the same instrument.

The DB-624 column is a medium polarity column and is the column used by the Metropolitan Water District of Southern California (MWDSC) for EPA Method 524.2 (P&T) for compliance VOC monitoring. An evaluation of this column compared to the DB-1 was necessary in order to determine whether it was suitable for the SPE method. It was determined, and discussed in further detail in the SPE section, that the DB-624 column was unsuitable for the SPE method.

A total ion chromatogram (TIC) comparison between the DB-624 column and a DB-1 column is shown in Figure 2. Because the DB-1 column showed significantly improved resolution of the analytes, it was determined that this column would be optimal for P&T analyses. One of the problems associated with the use of the DB-624 column was the coelution of some target compounds, such as chloropropanone and bromodichloromethane. This was not a problem with the DB-1 column.

Other Changes to P&T Method

Other changes to the P&T method included the use of only a selected list of VOCs combined with the other target DBPs. Initially the P&T method relied on the use of two separate sets of calibration standards and separate calibration curves. By paring down the VOC list to only the target VOCs of interest in this study and combining them with the target DBPs had some major advantages. One advantage was a simpler calibration step in which all of the P&T method compounds could be analyzed in a single P&T run. This eliminated the need to process sample data files twice. Also, the elimination of any coelution interferences between those VOCs that were part of a larger cocktail of analytes and some of the target DBPs. Some of the target DBPs that exhibited coelution problems were chloropropanone, bromodichloromethane, 1,1,1-trichloropropanone, chlorodiiodomethane, and bromochloroiodomethane. These compounds were difficult to separate from VOCs that were contained in the original cocktail of more than 60 VOC compounds. Chloropropanone and bromodichloromethane were resolved simply by changing to the DB-1 column.

Improved Temperature Program

An updated GC column temperature program was used beginning in January 2002. Figure 3 shows a TIC for a 10 µg/L standard analyzed with the updated column temperature program. This improvement allowed for better separation of the analyte peaks. The temperature program used was similar to the one used for the LLE and SPE analyses, except that a lower final temperature of 250 °C was used instead of 301 °C.

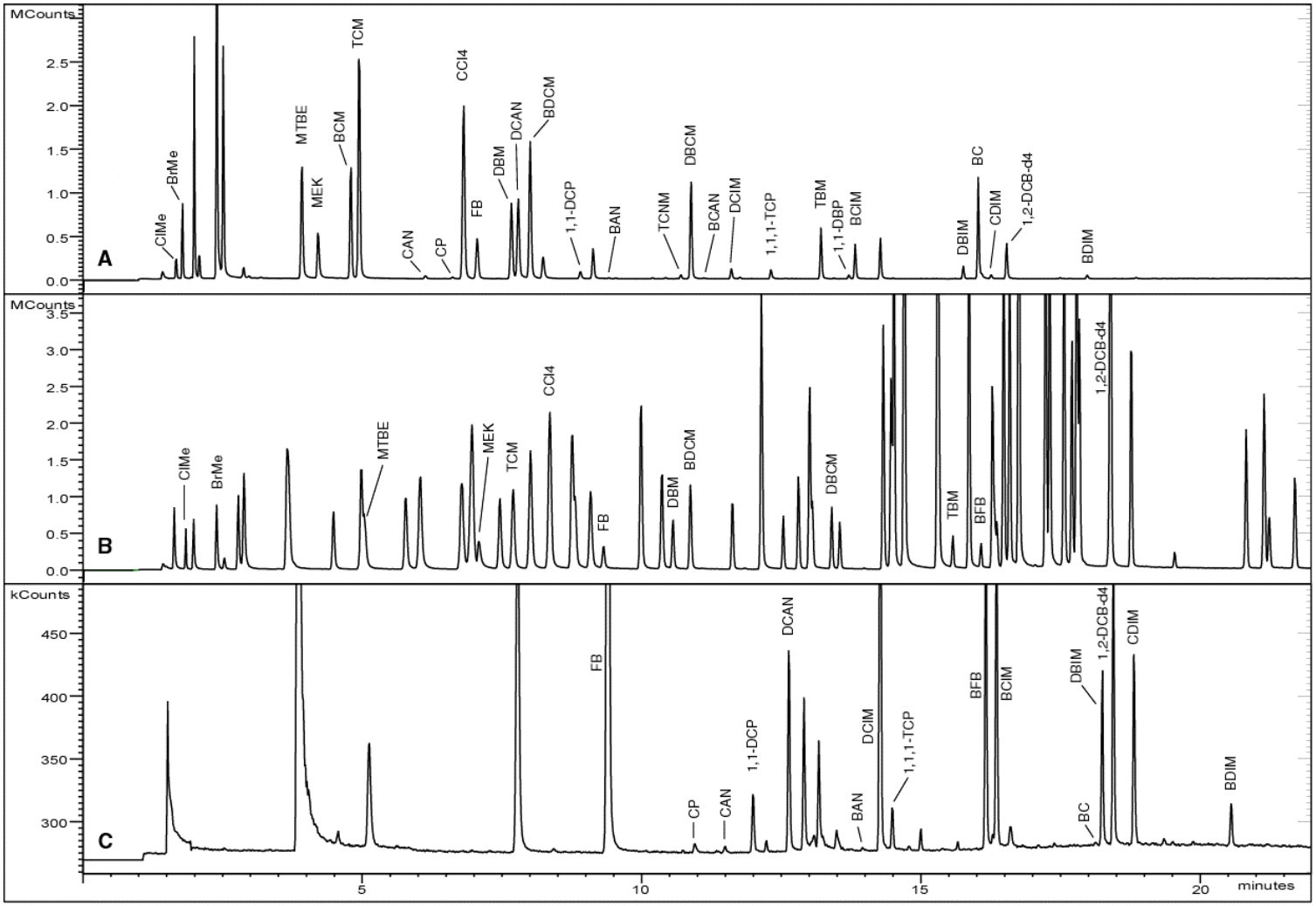

Figure 2. Comparison TIC between DB-624 and DB-1 columns for purge-and-trap analysis.
A) All target DBPs on DB-1 column; B) VOCs on DB-624 column; C) Target DBPs on DB-624 column.

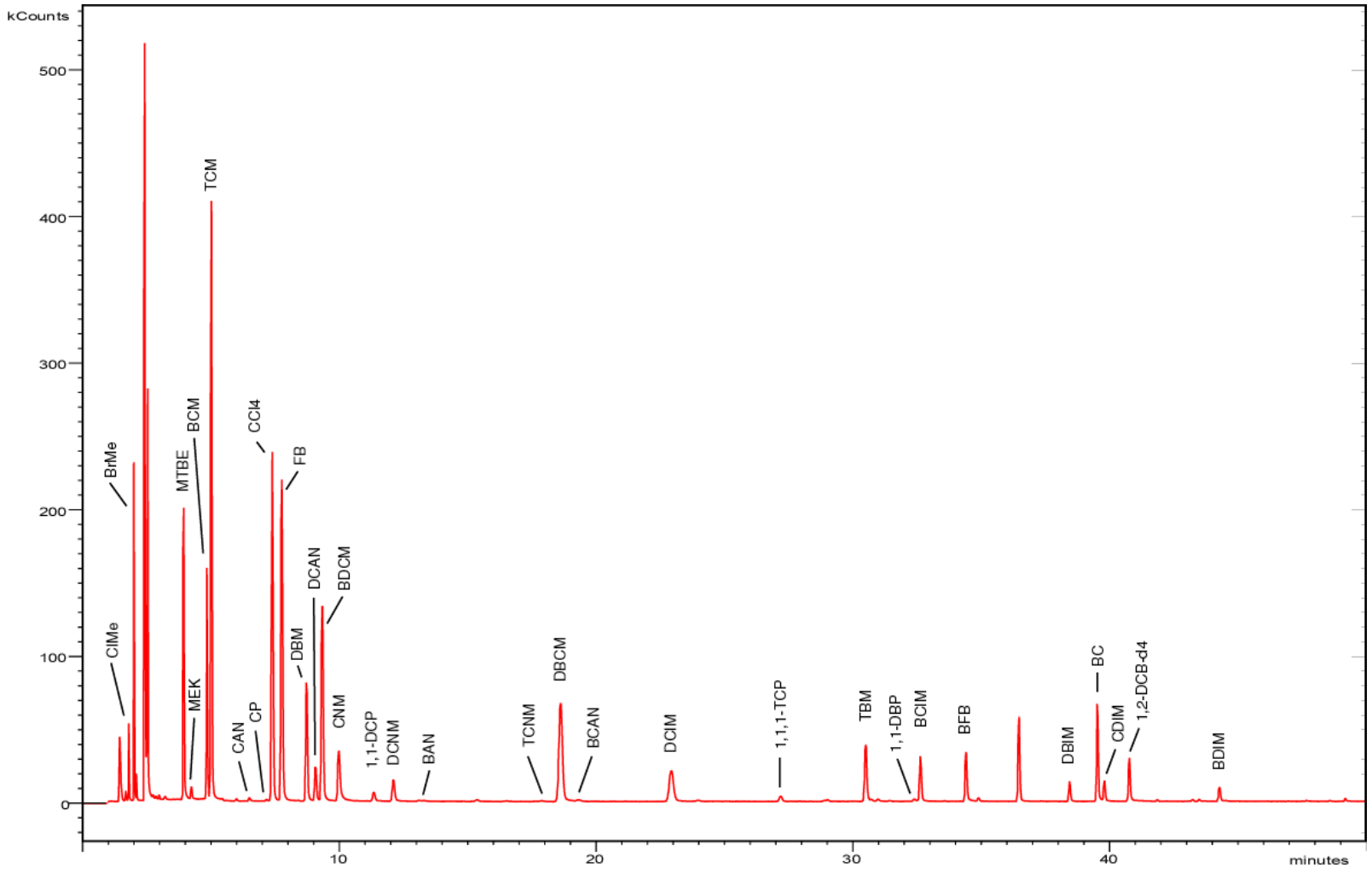

Figure 3. TIC for a 10 µg/L Purge-and-trap DBP/VOC standard on DB-1 column with extended column temperature program.

Holding Study

Sample stability data was used from previous work done using SPE or LLE methods, and was not repeated for the P&T analysis. The P&T analysis used the same sample bottles and preservation scheme as the SPE and LLE methods (ascorbic acid preserved) samples. To summarize these results by compound family:

VOCs -	Stable through Day 21.
THMs -	Stable through Day 21.
Iodo-THMs -	Stable through Day 21.
Haloacetonitriles -	Stable through Day 21
Chloropropanones -	Stable through Day 21.
Halonitromethanes -	Stable through Day 21.
Miscellaneous -	Benzyl chloride showed a slow decay.

Samples were generally analyzed within 2-3 days after receipt at MWDSC. This allowed for time to reanalyze samples if necessary and to allow for the instrument to be used for the SPE analyses later.

Improvements on the Saturn Ion-trap

One of the improvements made for the analysis of the P&T analytes was the use of multiple quantitation ions to increase the sensitivity. In previous analyses, a single ion was used to quantitate analyte peaks. The result of this change was an increase in selectivity for the target analytes.

CONCLUSIONS

EPA Method 524.2 was used as the basis for these analytes, but it was modified in such a way that an expanded list of compounds could be analyzed. The only real changes were the analytical column used and the column temperature program. The P&T concentrator parameters and the internal standard/surrogates remained the same. This P&T method was capable of analyzing for 32 DBPs as part of the Nationwide DBP Occurrence Study. Of those 32 compounds included in this method, 11 were originally analyzed as VOC compounds. The remaining 21 compounds represent additional compounds not normally associated with a P&T type of analysis. This P&T method allowed for confirmation of results obtained from SPE and LLE methods, as well as the solid phase microextraction method developed later.

REFERENCES

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